Bioresource Technology 245 (2017) 116–122

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Removal and recovery of acetic acid and two furans during sugar purification of simulated phenols-free biomass hydrolysates

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ARTICLE INFO

Keywords:
Acetic acid
Furans
Simulated biomass hydrolysates
Physical extraction
Emulsion liquid membrane
Adsorption

ABSTRACT

A cost-effective five-step sugar purification process involving simultaneous removal and recovery of fermentation inhibitors from biomass hydrolysates was first proposed here. Only the three separation steps (PB, PC and PD) in the process were investigated here. Furfural was selectively removed up to 98.4% from a simulated five-component hydrolysate in a cross-current three-stage extraction system with n-hexane. Most of acetic acid in a simulated four-component hydrolysate was selectively removed by emulsion liquid membrane, and it could be concentrated in the stripping solution up to 4.5 times its initial concentration in the feed solution. 5-Hydroxymethylfurfural was selectively removed from a simulated three-component hydrolysate in batch and continuous fixed-bed column adsorption systems with L-493 adsorbent. Also, 5-hydroxymethylfurfural could be concentrated to about 9 times its feed concentration in the continuous adsorption system through a fixed-bed column desorption experiment with aqueous ethanol solution. These results have shown that the proposed purification process was valid.

1. Introduction

Dilute sulfuric acid-catalyzed pretreatment of lignocellulosic biomass has been the most widely used method to produce xylose-rich liquid streams and enhance enzymatic digestibility of cellulose (Banerji et al., 2013; Davis et al., 2015; Lee and Park, 2016). The biomass pretreatment releases not only sugars into the liquid stream but also inhibiting compounds hampering microbial conversion of sugars to bio-alcohol (Arruda et al., 2009; Nam et al., 2011; Trinh et al., 2014). Theses inhibitors include aliphatic carboxylic acids (acetic, formic, levulinic acids), furans (furfural, 5-hydroxymethylfurfural), and lignin derivatives (mono- and poly-phenolic compounds) (Kim et al., 2013). Even though there have been many endeavors to find suitable sugar purification technologies to completely discard the inhibitors from biomass hydrolysates or to lower their concentrations in the hydrolysates to levels tolerated by microorganisms (Kudahettige-Nilsson et al., 2015; Maiti et al., 2012; Mateo et al., 2013; Soleimani et al., 2015), creating value from the inhibitors is still overlooked. If the inhibitors can be recovered during sugar purification steps of overall biomass-to-bio-alcohol conversion process, it would be more commercially viable.

Fig. 1 depicts a block flow diagram for the overall sugar purification process where all inhibitors and sulfuric acid can be removed from simulated biomass hydrolysates, which mimic hemicellulosic hydrolysates obtained by dilute sulfuric acid hydrolysis of lignocelluloses. Although the sugar purification process proposed here is not always available to treatment of all kinds of real hemicellulosic hydrolysates, it seems that one or more separation steps of the process or the whole process can be effectively used for development of new biomass-to bio-alcohol conversion process. As displayed in the first separation step (step PA) in the diagram, Lee and Park (2016) found that it was possible to selectively remove phenols from simulated biomass hydrolysates and end up getting phenols-free hydrolysates through batch or continuous fixed-bed column adsorption technologies using activated charcoal. The phenols-free hydrolysates were mainly composed of sulfuric acid, xylose, acetic acid, furfural, and 5-hydroxymethyl furfural. Therefore, the current work, only including the dotted box in Fig. 1, aimed to recover the most abundant and toxic aliphatic carboxylic acid (acetic acid) and two major furan derivatives (furfural and 5-hydroxymethylfurfural) from the simulated phenols-free biomass hydrolysates via the three separation steps, PB, PC, and PD. Since separation of sugar from sulfuric acid solution has been successfully achieved using emulsion liquid membrane (ELM) with amine extractants (Lee, 2014) and chromatography with polymer resins (Sun et al., 2015; Liu et al., 2016), the separation step PE specified in the diagram was no longer considered in this work.

2. Materials and methods

A simulated biomass hydrolysate used in step PB was composed of

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http://dx.doi.org/10.1016/j.biortech.2017.08.206
Received 24 July 2017; Received in revised form 30 August 2017; Accepted 31 August 2017
Available online 21 September 2017
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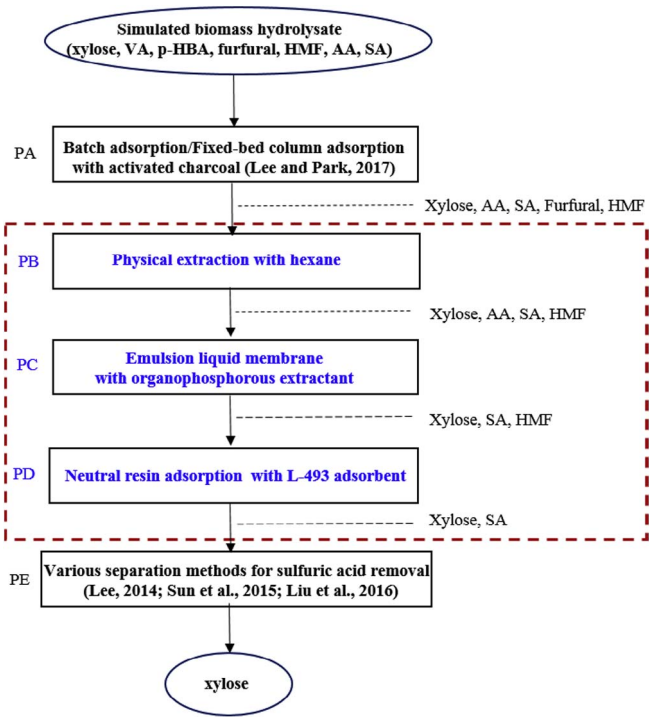

Fig. 1. A diagram of a five-step sugar purification process where all inhibitors and sulfuric acid can be removed or recovered from the simulated biomass hydrolysate (SA: sulfuric acid, AA: acetic acid, HMF: 5-hydroxymethylfurfural, p-HBA: 4-hydroxybenzoic acid, VA: vanillic acid).

xylose, sulfuric acid, furfural, 5-hydroxymethylfurfural (HMF), and acetic acid. The concentrations of xylose, sulfuric acid, acetic acid, furfural, and HMF in the hydrolysate were 100 mmol/L, 50 mmol/L, 50 mmol/L, 0.6 g/L, and 0.6 g/L, respectively. The concentrations of the five components in the simulated hydrolysate were not much different from those in the real hydrolysates presented by several researchers who pretreated lignocellulosic biomass by dilute sulfuric acid hydrolysis (Carvalheiro et al., 2005; Mussatto et al., 2004; Persson et al., 2002; Rodrigues et al., 2001; Villarreal et al., 2006).

2.1. Materials

D-xylose (98%) and furfural (98%) were purchased from Tokyo Chemical Industry. 5-hydroxymethylfurfural (98%) was purchased from Acros Organics. Sorbitan trioleate (Span 85) and trioctylphosphine oxide (99%, TOPO) were purchased from Sigma-Aldrich. Ethanol (99.9%) and n-hexane (96%) were purchased from Duksan Chemical. Sulfuric acid (97%) and acetic acid (99.7%) were purchased from Matsunoen Chemicals and Junsei Chemical, respectively. C9232 (Nonionic polyamine surfactant) was supplied by Infinium UK Ltd. All the chemicals were used without further purification. The resin Dowex Optipore L-493 (macroporous adsorbent with a matrix of styrene-divinylbenzene, L-493) was purchased from Sigma-Aldrich, which provided information about the particle size of 20–50 mesh, the pore volume of 1.16 cm^3/g, the mean pore size of 4.6 nm, the surface area of 1100 m^2/g, and the bulk density of 680 g/L. The resin were washed with ethanol at a 1:6 (w/v) ratio of resin to solvent in a shaker for 3 h. The solvent was separated from the resin by filtering with a filter paper. In the same way, the resin was washed with ultrapure water at a 1:6 (w/v) ratio of resin to water in the shaker for 0.5 h. After filtering the resin, it was dried in an oven at 80 °C for at least 10 h and used for the adsorption studies.

2.2. Methods

2.2.1. Physical extraction of furfural (Step PB)

Equilibrium experiments for physical extraction of furfural in pure water into pure n-hexane were conducted at varying volume ratios of the organic phase to the aqueous phase to find the partition coefficient of furfural between the two phases. The volume ratio, called a phase ratio below, ranged from 1 to 15.2, and the initial concentration of furfural in water was between 0.5 and 20 g/L. About 60 cm^3 of the organic and aqueous solutions in a 250-mL flask were vigorously shaken at 25 °C for 2 h. After separation of the two immiscible phases, the concentration of furfural in the aqueous phase was measured by a high performance liquid chromatography (HPLC) referred in Section 2.2.4.

In order to verify justification of step PB in Fig. 1, an aqueous quinary mixture composed of xylose, sulfuric acid, acetic acid, furfural, and HMF was used as a simulated biomass hydrolysate in a cross-current three-stage extraction system (Cox and Rydberg, 2004) where the aqueous raffinate leaving each extraction equilibrium stage was contacted successively with fresh n-hexane to give enhanced recovery of furfural from the hydrolysate. The phase ratio used in the three-stage extraction experiment kept constant at 4, 6 or 8 regardless of stage, and the other extraction method and conditions at each stage were the same as in one-stage single-component extraction experiments mentioned above.

2.2.2. Extraction of acetic acid by ELM (Step PC)

Since most of the furfural could be removed from the simulated phenols-free biomass hydrolysates during step PB, an aqueous quaternary mixture of xylose, sulfuric acid, acetic acid, and HMF was used as a feed solution of step PC. An organic solution (membrane phase) was prepared by dissolving a mixture of C9232 and Span 85 as an emulsifier and TOPO as an extractant in kerosene. An aqueous stripping solution was prepared by dissolving sodium carbonate in ultrapure water.

A water-in oil (W/O) emulsion was prepared by intensively mixing equal volumes of the organic and the stripping solutions by a homogenizer (T25, IKA Lab.) rotated at 12,000 rev/min for 10 min. 70 cm^3 of the W/O emulsion was dispersed in a batch-type stirred glass cell containing 420 cm^3 of the feed solution. Double emulsion formed was stirred at 360 rev/min throughout the ELM run and was maintained at 25 °C by water passing through a built-in water-jacket of the stirred cell. Its detailed description was given in the previous ELM works (Lee, 2014, 2015a). Samples were taken from the cell at given time intervals during the ELM run and then separated into the feed and the emulsion phases by filtration. A freezing and thaw method (Lee, 2014) was used to demulsify the spent emulsion and finally obtain the stripping solution when needed. The concentrations of each component in the feed and stripping solutions were determined by the HPLCs in Section 2.2.4.

2.2.3. Adsorption of HMF onto neutral polymer resin (Step PD)

The simulated biomass hydrolysate after step PC was almost an aqueous ternary mixture of HMF, xylose, and sulfuric acid, which represents a feed solution of step PD and also is called the simulated three-component biomass hydrolysate. In order to selectively remove and recover HMF from the aqueous feed solution, a neutral polymer resin (L-493) was chosen as an adsorbent because of its large surface area as well as nonpolar structure of its matrix (IJzer et al., 2015). The adsorbability of each component in the feed solution onto L-493 adsorbent was investigated through batch adsorption equilibrium experiments, where a given amount of L-493 was added to a 15 mL of the feed solution in a 100-mL Erlenmeyer flask. To ensure equilibrium, the flask was then placed and shaken in a mechanical shaker at 25 °C for 3 h. After separating the aqueous solution from L-493 using a filter paper, the concentration of each component in the solution was measured using the HPLCs below. Also, single-component (HMF)

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